

Application of Chemometrics to PFGSE NMR in Polymer Systems: Impact of Multi-exponential Relaxation on DECRA Analysis

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Abstract

The use of chemometrics and multivariate techniques has proven to be a powerful tool for the analysis of pulse field gradient spin echo (PFGSE) NMR spectral data. This is especially true in complex systems such as polymer systems. This laboratory has utilized a range of chemometric techniques, including direct exponential curve resolution (DECRA), component-resolved NMR (CORE), and non-linear multiple curve resolution (MCR) techniques for the analysis of PFGSE NMR data of aged polymer systems. DECRA provides very fast analysis speeds even for very large relaxation data sets: and is therefore almost always our first choice of analysis techniques. The advantages and limitations of the DECRA algorithm are addressed. In particular, the spectral distortions and errors introduced by the polydispersity of the self-diffusion decay coefficient were investigated. Many of our initial naïve assumptions about the effects of polydispersity on the chemometric analysis of PFGSE NMR data sets are are shown to be misguided.

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DECRA Theory

For 2 proportional data sets an unambiguous solution can be obtained!

$$\mathbf{A} = \mathbf{C}\mathbf{P}$$
$$\mathbf{B} = \mathbf{C}\alpha\mathbf{P}$$

M. Kubista, Chemometrics and Intel. Lab. Sys. 7 (1990) 273-279. W. Windig, B. Antalek, Chemometrics and Intel. Lab. Sys., 37 (1997) 241-254.

In order to solve this both **A**

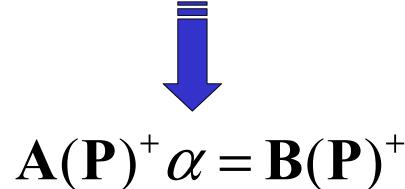
and **B** must be square!

Use a common space to

project both data files,

using SVD.

 α = diagonal scaling matrix



Generalized eigenvector Problem!

$$AZ\alpha = BZ$$

where

$$\mathbf{Z} = (\mathbf{P})^+$$

 $AZ\alpha = BZ$

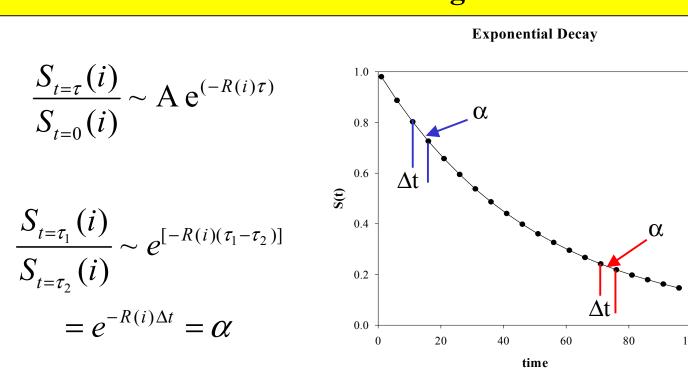
A = USV

Standard eigenvector problem!

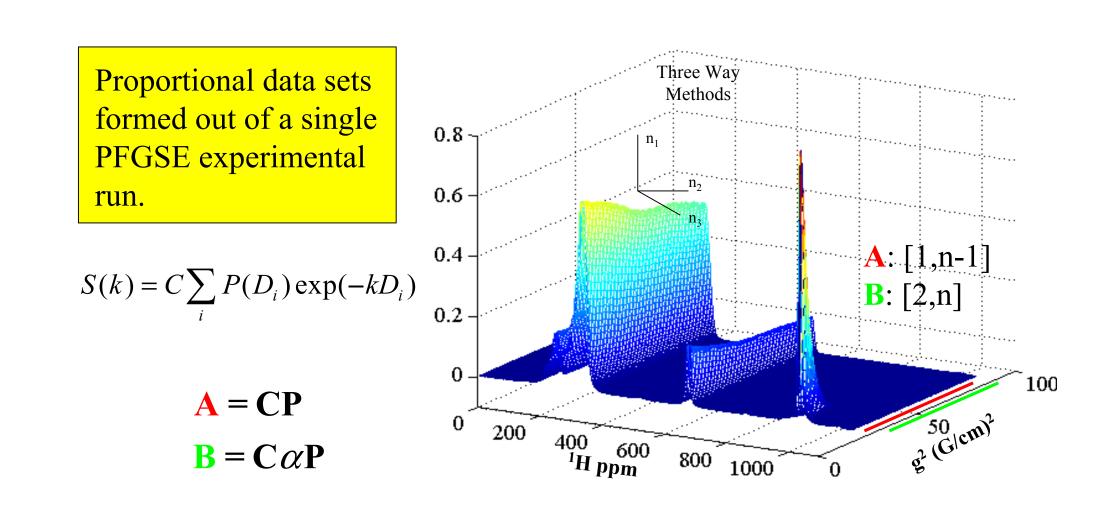
$$\mathbf{Z}^* \boldsymbol{\alpha} = \left(\overline{\mathbf{U}}^{\mathrm{T}} \mathbf{B} \overline{\mathbf{V}} \overline{\mathbf{S}}^{-1} \right) \mathbf{Z}^*,$$

$$\mathbf{Z}^* = \overline{\mathbf{S}} \overline{\mathbf{V}}^{\mathrm{T}} \mathbf{Z}$$

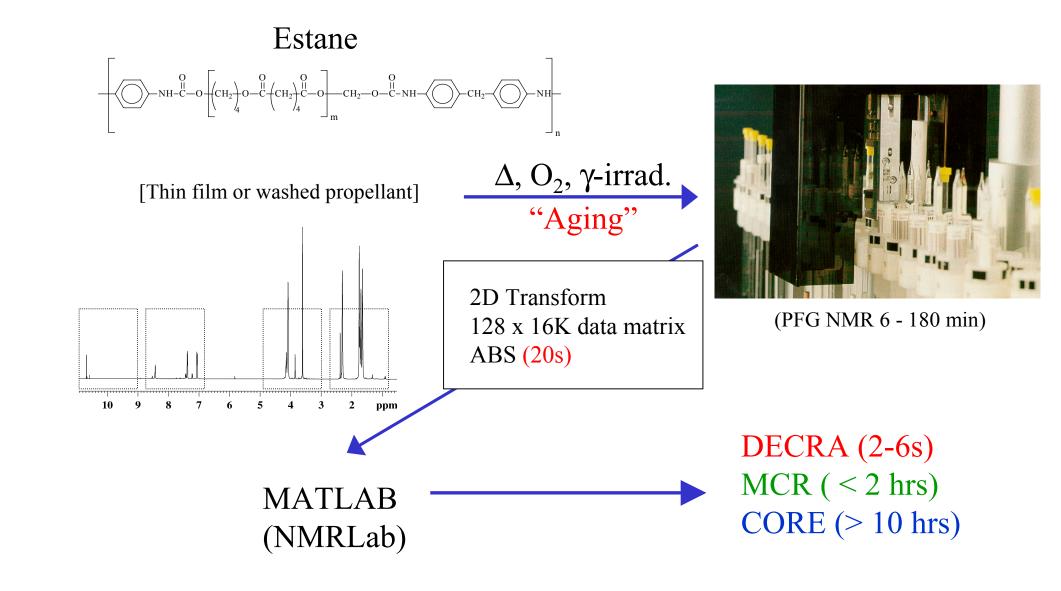
For equally spaced data along exponential decay, the proportionality constant α is the same for any pair of related data. In this case the data matrices A and B can be formed from a single data set!

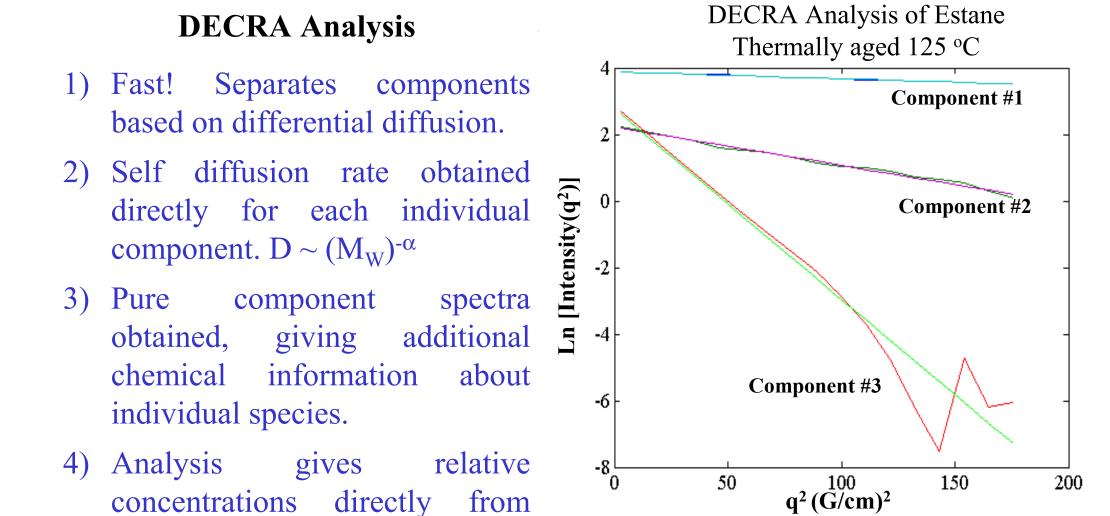


PFGSE Analysis of Polymers

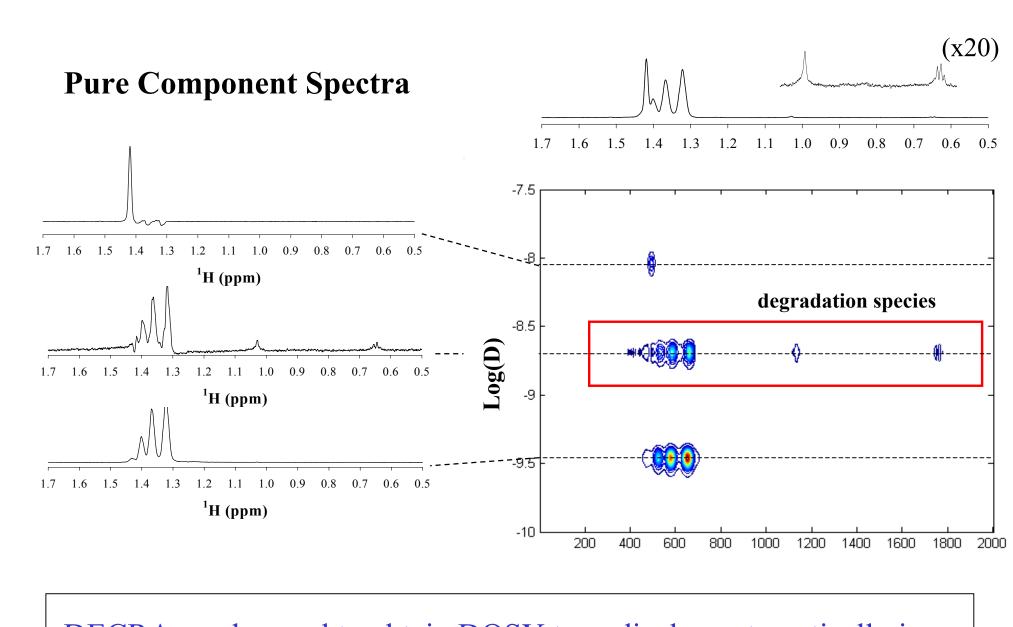


Estane/Antioxidant Studies



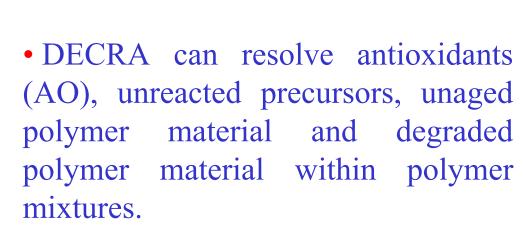


eigenvalues.

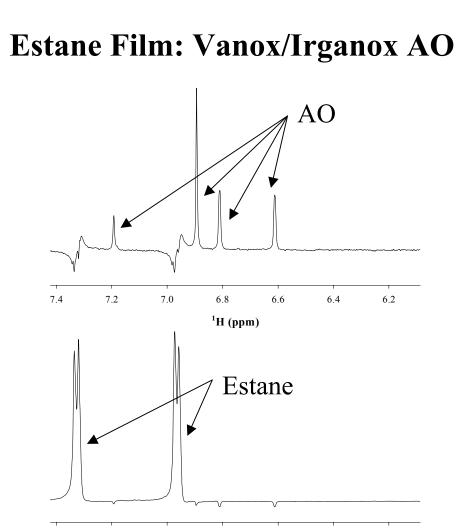


DECRA can be used to obtain DOSY type display automatically in a matter of seconds via MATLAB on a PC.

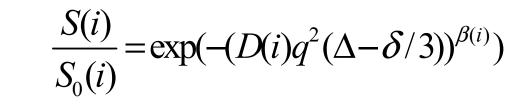
Polydispersity Effects

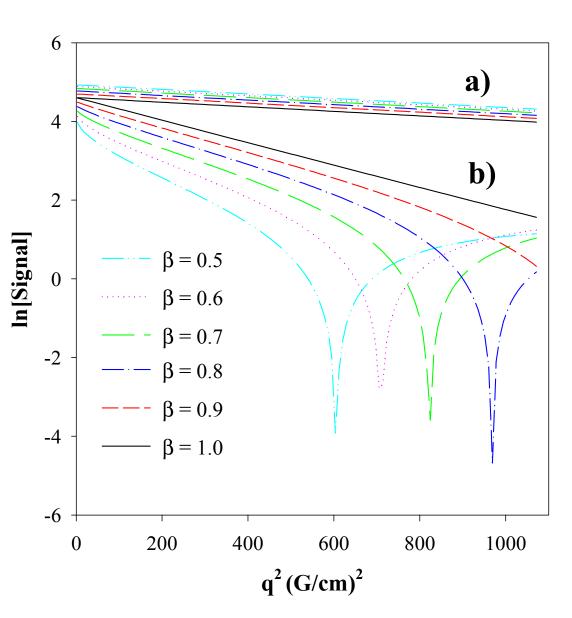


- Some pure component spectral "mixing" observed.
- Is this "mixing" an effect of multicomponent relaxation? What are the impacts of polydispersity on the DECRA analysis. Proportionality assumption not fulfilled.
- Simulations of PFG data sets with summations of decay constants were created to address these issues.



Kohlrausch-Williams-Watts (KWW) distribution



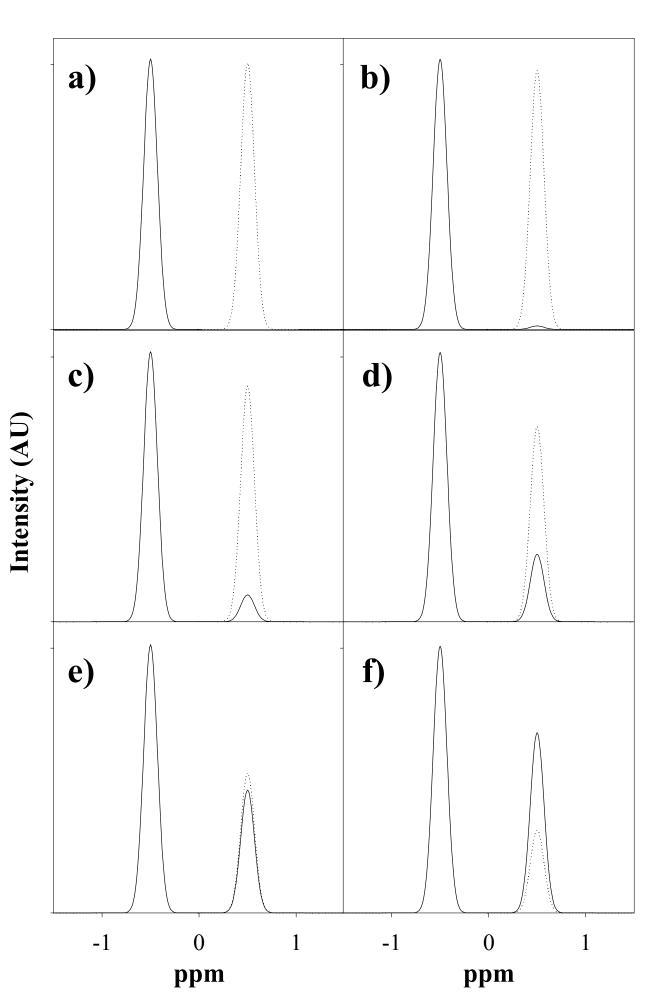


Simulated Summation of Diffusion Distribution

$$S(k) = C\sum_{i} P(D_{i}) \exp(-kD_{i})$$

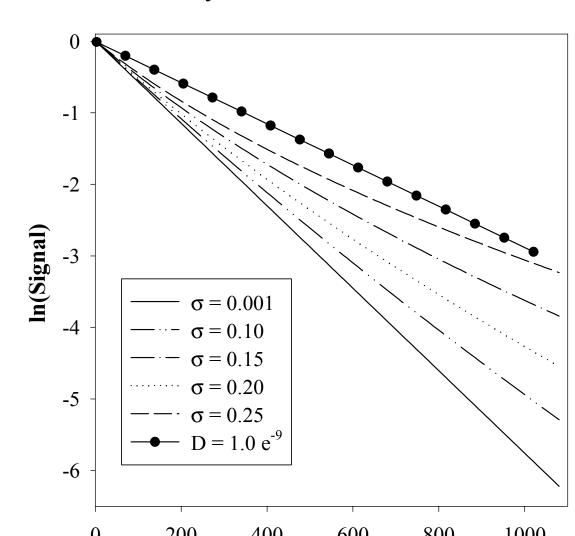
Log – Normal Distribution

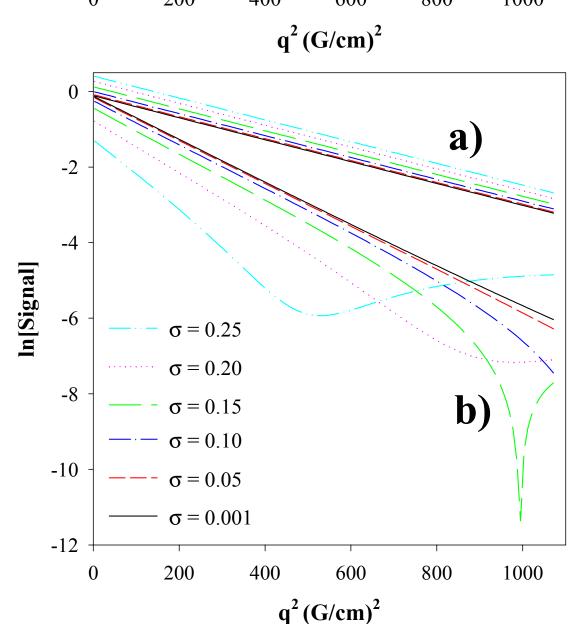
$$P(D) = \frac{1}{2\sigma\sqrt{2\pi}} \exp\left(-\frac{\left[\ln(D) - \ln(D_0)\right]^2}{2\sigma^2}\right)$$



Pure component line shapes for increasing D distribution: a) $\sigma = 0.001$, b) $\sigma = 0.05$, c) σ = 0.10, d) $\sigma = 0.15$, e) $\sigma = 0.20$, f) $\sigma = 0.25$







Conclusions

- "Mixing" impacts BOTH components in the spectra not just the multi-exponential portions. Overall error of the spectra NOT a good indicator of fit.
- Diffusion constants of single-exponential component NOT affected. Multi-exponential component error dependent on polydispersity.
- Unique "error signature" observed experimentally in some systems.
- •Lineshape variation controls number of relevant eigen values

